

Commercial Applications of Gold Catalysts for CO Oxidation – Performance, Deactivation, Regeneration.

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Introduction

Supported gold nano-particles on metal oxide supports have been recognized as effective low temperature CO oxidation catalysts. Although the use of gold catalysts in short term room temperature applications holds promise (e.g. escape respirators [1]) the use of gold in long term applications (e.g. air-conditioning, PROX, CO₂ lasers) remains less certain. In order to be commercially viable gold catalysts must meet or exceed a specified minimum service life for each application before disposal or possible regeneration.

Gold catalyst deactivation has been reported by those skilled in the art [2], however very few systematic studies at viable commercial conditions (gas composition, GHSV) have been conducted. Catalyst regeneration has also been reported [3] – however confusing and even contradictory results have been obtained, with a certain degree of regeneration possible by exposing catalysts to oxidizing or reducing atmospheres and certain heat treatment methods.

In light of the above, AuTEK has tested its gold catalyst systems under simulated commercial conditions using synthetic gas feedstock's. The two systems of interest are an unconventional PROX system, consisting of the removal of CO from 'dirty' hydrogen, and an air-conditioning application. Catalyst deactivation is indeed observed in each system and a systematic study was attempted to explain the source(s) of deactivation. Methods of catalyst regeneration were also employed with varying degrees of success.

Materials and Methods

Various gold loaded Au/TiO₂ (Degussa P25) and Au/ZnO (Süd-Chemie G72D) catalysts were synthesized by employing the deposition precipitation technique. Flow experiments were conducted in a continuous flow micro fixed bed reactor, under a variety of conditions depending on the system employed. 'Standard conditions' are: PROX = 80ppm CO, 2% air in H₂, 2 000 l/g_{cat}/hr, adiabatic, 0% RH; Air-conditioning = 75ppm CO, 240ppm CO₂ in air, 1 000 l/g_{cat}/hr, adiabatic, 14% RH.

Results and Discussion

The seemingly contradictory positive and negative effects of moisture have been widely reported in literature [4]. In terms of the air-conditioning application, systematic studies show that a promotional effect of water is seen when catalyst surface is hot, either by external heating or the heat generated by the exothermic CO oxidation reaction. In contrast, catalysts that show poor activity cannot generate enough heat to prevent water condensation on their surfaces. Despite eliminating rapid water induced deactivation (catalysts heating, 0%RH) a 'slow' deactivation is still observed. DRIFTS analysis points to the formation and accumulation of carbonates as being responsible for this phenomenon. Limited regeneration by ozonation, irradiation and heat treatment methods will also be discussed.

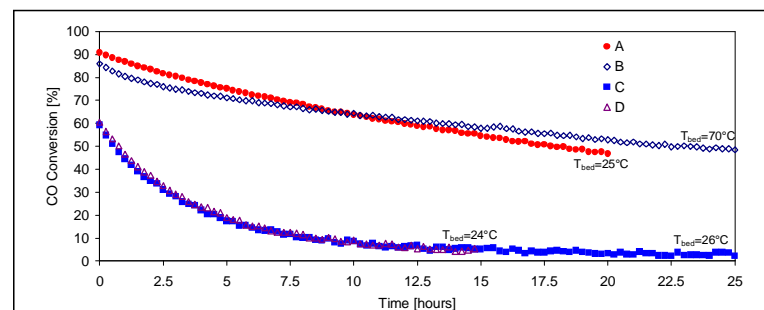


Figure 1. Air-conditioning 3wt% Au/TiO₂ - A) 0% RH, B) 70°C, C) STD., D) 0% CO₂

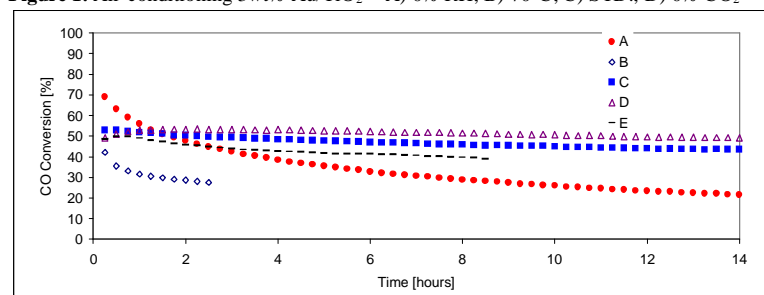


Figure 2. PROX 3wt% Au/TiO₂ - A) STD., B) H₂ pre-treatment, C) 100°C, D) 100°C + 0.42 vol% H₂O, E) 100°C + 3.1 vol% H₂O

Similarly, under PROX conditions water induced deactivation is also present, albeit in this instance by in-situ water formation (due to hydrogen oxidation). Rapid water induced deactivation may be eliminated by heating, although once again a 'slow' deactivation is observed. While it is proposed that gold reduction may play a role in deactivation, with limited regeneration made possible by oxidizing treatments (e.g. O₂ and O₃), the formation of carbonate species cannot be excluded.

Significance

The use of gold catalysts under simulated commercial PROX and air-conditioning conditions shows that catalyst deactivation is an issue.

References

1. Wood, T., Chamberlain, C., Siedle, et al., Proc. GOLD 2006, Limerick, Sept. 2006.
2. Schubert, M.M., Venugopal, A, Kahllich, M, et al., *J.Catal.* 222, 32 (2004).
3. Konova, P., Naydenov, A., Venkov, C., et al., *J. Mol Catal* 213, 235 (2004).
4. Bond, G.C., Louis, C., Thompson, D. in "Catalysis by Gold" (G.J. Hutchings, Ed.) Vol. 6 p. 166. Imperial College Press, London, 2006.